Polymer Adsorption on Disordered Substrate

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Abstract

We analyze the recently proposed "pattern-matching" phase of a Gaussian random heteropolymer adsorbed on a disordered substrate [S. Srebnik, A.K. Chakraborty and E.I. Shakhnovich, Phys. Rev. Lett. **77**, 3157 (1996)]. By mapping the problem to that of a directed homopolymer in higher-dimensional random media, we show that the pattern-matching phase is asymptotically weakly unstable, and the large scale properties of the system are given by that of an adsorbed homopolymer.

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In a recent letter [1], Srebnik, Chakraborty and Shakhnovich (SCS) presented an interesting study of the adsorption of a *Gaussian* random heteropolymer (RHP) onto a disordered 2D substrate. SCS used a mean-field analysis of a replica calculation to show that for large substrate disorders, the polymer is adsorbed onto the substrate and forms a *glass* phase which is dominated by the matching of "patterns" of the RHP and the substrate. In this comment, we describe how such a pattern matching phase might arise in principle, and show that it cannot exist for the model considered by SCS.

We recall the model RHP Hamiltonian used in Ref. [1]

$$\beta\mathcal{H} = \int_0^N dn \left\{ \dot{\mathbf{r}}^2 + k\left[\mathbf{r}(n)\right]\theta(n)U(z(n)) \right\} \tag{1}$$

where $\mathbf{r}(n) = (\mathbf{r}_{||}(n), z(n)) \in \Re^3$ and $\theta(n) \in \{\pm 1\}$ denote respectively the position and "charge" of the nth monomer, $\dot{\mathbf{r}} \equiv d\mathbf{r}/dn$, and $U(z)$ is a short-ranged substrate potential (taken here to be of unit strength). The RHP is assumed to be charge-neutral on average, with short-range correlations $\overline{\theta(n)\theta(n')} = \sigma_2^2\,\delta(n - n')$. The substrate potential is also assumed to be short-range correlated, with $\overline{k(\mathbf{r})k(\mathbf{r}')} = \sigma_1^2\,\delta^2(\mathbf{r}_{||} - \mathbf{r}'_{||})$.

Consider first the case of strong disorders ($\sigma_1 \cdot \sigma_2 \gg 1$) such that the polymer is tightly bounded to the substrate. In this limit, the polymer conformation is controlled by the effective random potential $W(\mathbf{r}_{||}, n) \equiv \theta(n)\,k(\mathbf{r}_{||})$, whose leading moments are $\overline{W} = 0$ and $\overline{W(\mathbf{r}_{||}, n)W(\mathbf{r}'_{||}, n')} = \sigma_1^2\sigma_2^2\,\delta^2(\mathbf{r}_{||} - \mathbf{r}'_{||})\,\delta(n - n')$. The explicit n-dependence in W makes the problem distinct from homopolymer adsorption, and is the key ingredient to the generation of heteropolymer effects such as pattern matching. Properties of the conjectured pattern matching phase can be obtained by viewing the Gaussian RHP as a $(2+1)$-dimensional *directed polymer* in the random potential $W(\mathbf{r}_{||}, n)$; the latter problem has been characterized extensively [2]: For example, the radius-of-gyration exponent is $\nu \approx 5/8$, and the energy cost δE of confining the polymer to a region of linear size $\ell \ll N^\nu$ crosses over from the thermal form $\delta E \sim 1/\ell^2$ to $\delta E \sim \sigma_1\sigma_2/\ell^\omega$ for large ℓ, with $\omega = (2 - 2\nu)/\nu \approx 1.2$.

However, due to the fact that the effective potential W is a product of two *lower* dimensional random variables, $\theta(n)$ and $k(\mathbf{r})$, W cannot truly be a 3-dimensional random variable.

It is therefore important to check whether the parasitic long-range correlations in W (to be given below) would modify the asymptotic behaviors, i.e., whether they are relevant in the renormalization-group sense. The relevancy of parasitic correlations depends on the context of the problem. We have found that such correlations are irrelevant in a number of recent studies (see, e.g. Ref. [3]). Below, we show that such correlations are instead *relevant* for the problem at hand.

Long-range correlations are manifested in the higher moments of W. For instance, the four-point correlator

$$\overline{W(\mathbf{r}_{||}, n) W(\mathbf{r}_{||}, n') W(\mathbf{r}'_{||}, n) W(\mathbf{r}'_{||}, n')} = \overline{k^2(\mathbf{r}_{||}) k^2(\mathbf{r}'_{||})}$$

is independent of n since $\theta^2(n) = 1$. This suggests the generation of an n-independent potential, $V(\mathbf{r}_{||}) \sim k^2(\mathbf{r}_{||})$, the existence of which can also be verified for a generic distribution of θ and is not limited to $\theta \in \{\pm 1\}$. The behavior of the polymer is therefore determined by the combined effect of the potentials V and W which compete with each other: $V(\mathbf{r}_{||})$ attempts to localize the polymer to a region of the substrate where V is large and negative, while $W(\mathbf{r}_{||}, n)$ delocalizes the polymer (with $\nu > 1/2$) and encourages "pattern matching". Quantitatively, an energy gain of the order $\delta V \sim \sigma_1^2/\ell^{d_{||}/2} = \sigma_1^2/\ell$ is obtained by localizing the polymer within a scale ℓ in a favorable region of V. Comparing δV with the confinement cost δE given above for the pattern matched phase, one sees that localization effects always dominate at large scales. Optimizing the total energy yields a confinement scale $\ell \sim (\sigma_2/\sigma_1)^{1/(\omega-1)}$. Thus, heterogeneity is asymptotically *irrelevant*, and the interesting pattern matching phase cannot exist for long Gaussian polymers exceeding a crossover length $N_\times = \ell^{1/\nu}$.

So far, we discussed only the strong-adsorption limit where the polymer lies completely on the surface. For weaker adsorptions, segments of the polymer will escape from the surface (for both energetic and entropic reasons), forming a layer of loops. However, as long as the loops have finite lengths (which is the case in the adsorbed phase by definition), the problem with/without loops should become equivalent upon coarse graining beyond the loop size.

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We thus expect the absence of the pattern-matching phase throughout the adsorbed phase for the Gaussian polymer. Extensive numerical calculations of the full model (1) strongly supports the above conclusion and will be presented elsewhere.

REFERENCES

[1] S. Srebnik, A.K. Chakraborty and E.I. Shakhnovich, Phys. Rev. Lett. **77**, 3157 (1996).

[2] See for example, T. Halpin-Healy and Y.-C. Zhang, Phys. Rep. **254**, 215 (1995); and references therein.

[3] D. Cule and T. Hwa, preprint (cond-mat/9706262).